

CLAIMS

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1. A process for carrying out impregnation and/or for preparing a coating which gives release and is leaktight employed at the engine block/cylinder head interface of engines and applied in particular to sheet gaskets, in particular cylinder head gaskets, characterized in that it consists essentially:

10 1 - in employing a silicone composition comprising:

-A- 100 parts by weight of at least one polyorganosiloxane (POS) crosslinkable by the cationic and/or radical route and via crosslinking functional groups (CFGs), these CFGs being identical to or 15 different from one another and being chosen from those comprising at least one functional unit of heterocyclic nature having one or more electron-donating atoms and/or from those which are ethylenically unsaturated and substituted by at least one electron-donating atom which enhances the 20 basicity of the π system;

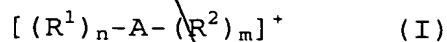
25 -B- from 0.01 to 10 parts by weight of at

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least one initiator salt (PI) formed by a borate of an onium of an element from groups 15 to 17 of the Periodic Classification [Chem. & Eng. News, Vol. 63, No. 5, 26 of February 4, 1985] or of an organometallic complex of an element from groups 4 to 10 of the Periodic Classification (same reference),

10 the cationic entity of said borate being chosen from:

(1) - onium salts of formula (I):



15 in which formula:

- A represents an element from groups 15 to 17;
- R^1 represents a C_6-C_{20} carbocyclic or heterocyclic aryl radical, it being possible for said heterocyclic radical to comprise nitrogen or sulfur as heteroelements;
- R^2 represents R^1 or a linear or branched C_1-C_{30} alkyl or alkenyl radical; said R^1 and R^2 radicals

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optionally being substituted by a C₁-C₂₅ alkoxy, C₁-C₂₅ alkyl, nitro, chloro, bromo, cyano, carboxy, ester or mercapto group,

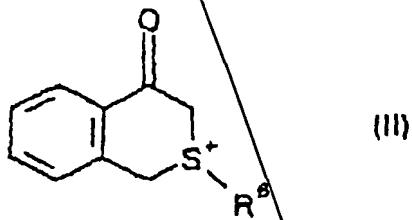
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- n is an integer ranging from 1 to v + 1, v being the valency of the element A,
- m is an integer ranging from 0 to v - 1, with n + m = v + 1,

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(2) - the oxoisothiocromanium salts having the formula:

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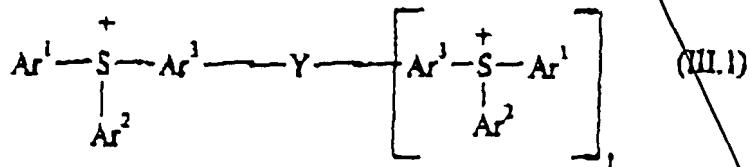
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where the R⁶ radical represents a linear or branched C₁-C₂₀ alkyl radical;

(3) - sulfonium salts where the cationic entity comprises:

→ 3.1. at least one polysulfonium species of formula III.1

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in which:

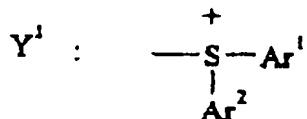
- the Ar^1 symbols, which can be identical to or
 different from one another, each represent a
 5 monovalent phenyl or naphthyl radical optionally
 substituted with one or more radicals chosen from:
 a linear or branched $\text{C}_1\text{-C}_{12}$ alkyl radical, a linear
 or branched $\text{C}_1\text{-C}_{12}$ alkoxy radical, a halogen atom,
 an -OH group, a -COOH group, a -COO-alkyl ester
 10 group, where the alkyl part is a linear or
 branched $\text{C}_1\text{-C}_{12}$ residue, and a group of formula $-\text{Y}^4-$
 Ar^2 , where the Y^4 and Ar^2 symbols have the meanings
 given immediately below,
 15 *A_{cont}* - the Ar^2 symbols, which can be identical to or
 different from one another or Ar^1 , each represent a
 monovalent phenyl or naphthyl radical optionally
 substituted with one or more radicals chosen from:
 a linear or branched $\text{C}_1\text{-C}_{12}$ alkyl radical, a linear
 or branched $\text{C}_1\text{-C}_{12}$ alkoxy radical, a halogen atom,
 20 an -OH group, a -COOH group or a -COO-alkyl ester
 group, where the alkyl part is a linear or
 branched $\text{C}_1\text{-C}_{12}$ residue,
 - the Ar^3 symbols, which can be identical to or
 different from one another, each represent a
 25 divalent phenylene or naphthylene radical
 optionally substituted with one or more radicals

chosen from: a linear or branched C₁-C₁₂ alkyl radical, a linear or branched C₁-C₁₂ alkoxy radical, a halogen atom, an -OH group, a -COOH group or a -COO-alkyl ester group, where the alkyl part is a linear or branched C₁-C₁₂ residue,

5 - t is an integer equal to 0 or 1,

with the additional conditions according to which:

+ when t = 0, the Y symbol is then a Y¹ monovalent radical representing the group of formula:



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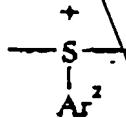
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where the Ar¹ and Ar² symbols have the meanings given above,

+ when t = 1:

* on the one hand, the Y symbol is then a divalent radical having the following meanings Y² to Y⁴:

• Y²: a group of formula:



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where the Ar² symbol has the meanings given above,

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• Y³: a single valency bond,

• Y⁴: a divalent residue chosen from:



a linear or branched C₁-C₁₂ alkylene residue and a residue of formula -Si(CH₃)₂O-,

* on the other hand, solely in the case where the Y symbol represents Y³ or Y⁴, the Ar¹ and Ar² (terminal) radicals have, in addition to the meanings given above, the possibility of being connected to one another via the Y' residue consisting in Y'¹, a single valency bond, or in Y'², a divalent residue chosen from the residues cited with respect to the definition of Y⁴, which is inserted between the carbon atoms, facing each other, situated on each aromatic ring in the ortho position with respect to the carbon atom directly bonded to the S⁺ cation;

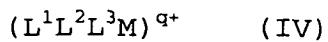
→ 3.2. and/or at least one monosulfonium species having a single S⁺ cationic center per mole of cation and consisting, in the majority of cases, in species of formula:

$$\begin{array}{c} + \\ \text{Ar}' \text{---} \text{S} \text{---} \text{Ar}' \\ | \\ \text{Ar}^2 \end{array} \quad (\text{III.2})$$

25 in which Ar^1 and Ar^2 have the meanings given above with

respect to the formula (III.1), including the possibility of connecting directly between them only one of the Ar^1 radicals to Ar^2 according to the way indicated above with respect to the definition of the 5 additional condition in force when $t=1$ in the formula (II) involving the Y' residue;

(4) organometallic salts of formula (IV):



in which formula:

10 • M represents a metal from group 4 to 10,
 • L^1 represents 1 ligand bonded to the metal M via π electrons, which ligand is chosen from η^3 -alkyl, η^5 -cyclopentadienyl and η^7 -cycloheptatrienyl ligands and η^6 -aromatic compounds chosen from optionally substituted η^6 -benzene ligands and compounds having from 2 to 4 condensed rings, each ring being capable of contributing to the valency layer of the metal M via 3 to 8 π electrons,

15 • L^2 represents a ligand bonded to the metal M via π electrons, which ligand is chosen from η^7 -cycloheptatrienyl ligands and η^6 -aromatic compounds chosen from optionally substituted η^6 -benzene ligands and compounds having from 2 to 4 condensed rings, each ring being capable of contributing to the valency layer of the

20 • L^3 represents a ligand bonded to the metal M via π electrons, which ligand is chosen from η^5 -cyclopentadienyl ligands and η^6 -aromatic compounds chosen from optionally substituted η^6 -benzene ligands and compounds having from 2 to 4 condensed rings, each ring being capable of contributing to the valency layer of the

25 • L^4 represents a ligand bonded to the metal M via π electrons, which ligand is chosen from η^5 -cyclopentadienyl ligands and η^6 -aromatic compounds chosen from optionally substituted η^6 -benzene ligands and compounds having from 2 to 4 condensed rings, each ring being capable of contributing to the valency layer of the

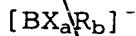
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metal M via 6 or 7 π electrons.

- L^3 represents from 0 to 3 identical or different ligands bonded to the metal M via σ electrons, which ligand(s) is (are) chosen from CO and NO_2^+ ; the total electronic charge q of the complex to which L^1 , L^2 and L^3 and the ionic charge of the metal M contribute being positive and equal to 1 or 2;

the anionic entity [lacuna] borate having the formula:



in which formula:

- a and b are integers ranging from 0 to 3 for a and from 1 to 4 for b, with $a + b = 4$.

- the x symbols represent:

- * a halogen atom with $a = 0$ to 3,
- * an OH functional group with $a = 0$ to 2.

- the R symbols are identical or different and represent:

- ▶ a phenyl radical substituted by at least one electron-withdrawing group and/or by at least 2 halogen atoms, this being when the cationic entity is an onium of an element from groups 15 to 17,

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▶ a phenyl radical substituted by at least one electron-withdrawing element or group, this being when the cationic entity is an organometallic complex of an element from groups 4 to 10,

▶ an aryl radical comprising at least two aromatic nuclei, which is optionally substituted by at least one electron-withdrawing element or group, whatever the cationic entity;

-C- 1 to 50 parts by weight of at least one reactive diluent consisting in a nonorganosilicon organosilicon or organic compound comprising, in its structure, at least one CFG as defined above and optionally at least one secondary functional group (SFG) other than a CFG but capable of reacting chemically with a CFG;

-D- 0 to 10 parts by weight of at least one pigment;

-E- 0 to 100 parts by weight of a filler of inorganic nature;

-F- 0 to 10 parts by weight of at least one photosensitizer;

-G- 0 to 10^{-2} part by weight of a stabilizer

PROPOSED EDITION

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consisting in at least one stabilizing amine agent,

-H- 0 to 5 parts by weight of an adhesion promoter;

5 2 - in applying this composition to a support (cylinder head sheet gasket or cylinder head/engine block interface), and

10 3 - in crosslinking the applied composition by photochemical and/or thermal activation and/or under an electron beam.

2. The process as claimed in claim 1, characterized in that the support is a metal cylinder head gasket.

15 3. The process as claimed in claim 2, characterized in that the support is a metal multilayer cylinder head gasket and in that a coating is formed on at least one of the faces of at least one of the layers composing the metal multilayer cylinder head gasket.

4. The process as claimed in any one of 20 claims 1 to 3, characterized in that the functional units included in the CFG groups are selected from the group of following units:

- an ethylenically unsaturated and activated functional group,

25 - epoxide,

- oxethane,

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- and their mixtures,

and in that the functional units included in the optional SFG groups are selected from the group of following units:

5 - hydroxyl,
 - alkoxy,
 - carboxyl,
 - and their mixtures.

5. The process as claimed in any one of
 10 claims 1 to 4, characterized in that the POSSs A are epoxysilicones and/or vinyl ether silicones which are:
 → either linear or substantially linear and composed of units of formula (I), terminated by units of formula (II),
 → or cyclic and composed of units of formula (II):



in which formulae:

20 • the R^3 symbols are alike or different and represent:
 - either a hydroxyl radical,
 - or a linear or branched $\text{C}_1\text{-C}_{18}$ alkyl radical which is optionally substituted by one or more halogens and/or a hydroxyl radical,
 - or a $\text{C}_2\text{-C}_8$ alkenyl radical,

- or an optionally substituted C₅-C₈ cycloalkyl radical,
- or an aryl or aralkyl radical which is optionally substituted by halogens and/or alkoxyls,

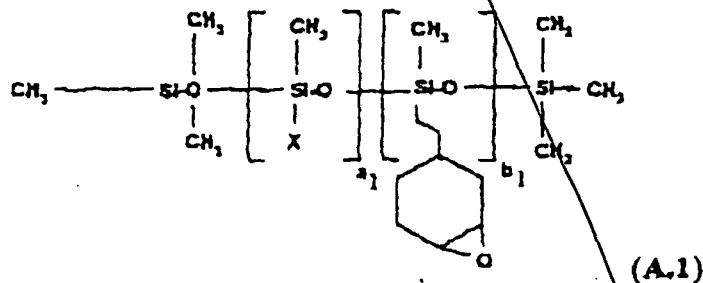
5 • the Z symbols are alike or different and represent:

- either the R³ radical,
- or a CFG group corresponding to an epoxide or vinyl ether residue connected to the silicon

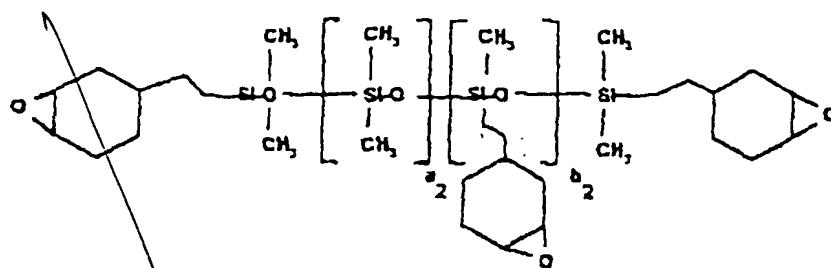
10 via a divalent radical comprising from 2 to 20 carbon atoms and optionally comprising a heteroatom,

15 at least one of the Z symbols corresponding to a CFG group.

15 6. The process as claimed in any one of claims 1 to 5, characterized in that the POSS A are epoxysilicones of formula (A.1), (A.2) and (A.3):



20 with X = CH₃; phenyl; C₅-C₈ cycloalkyl; C₁-C₁₈ alkyl; C₂-C₈ alkenyl; -OH; H; -CH₂-CH₂-CH₂-OH; -CH₂-CH₂-CF₃ or -(CH₂)_n-CF₃, n = 1 to 20;



(A.2)

- a_1 , a_2 , b_1 and b_2 being defined as follows in these formulae (A.1) and (A.2)

$$1 \leq a_1, a_2$$

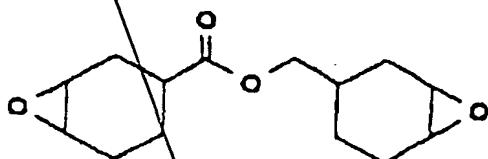
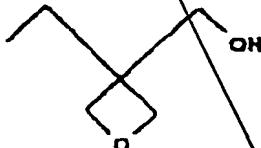
$$1 \leq b_1, b_2$$

5 - a_2 and b_2 being = 0 in the formula (A.2) to give the epoxidized disiloxane (A.3).

7. The process as claimed in any one of claims 1 to 6, characterized in that the reactive diluent(s) C is (are) chosen:

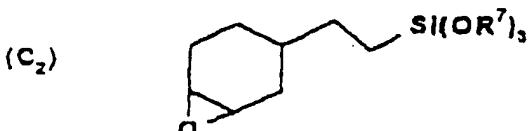
10 → from the nonorganosilicon organic compounds (C₁) possessing CFG + optionally SFG reactive groups having the following formulae:

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(C₁)(C₁')(C₁'')(C₁''')

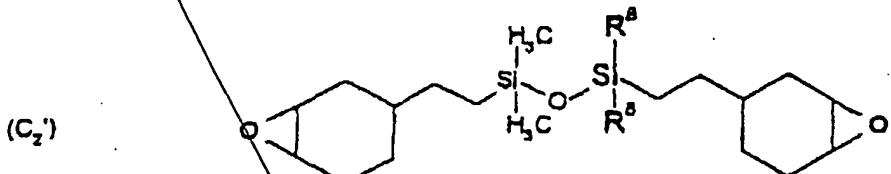
→ and/or from the organosilicon compounds (C₂) possessing CFG + optionally SFG reactive groups having the following formulae:

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with $R^7 = C_1-C_{10}$ alkyl,

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with R^8 independently representing a C_1-C_{10} alkyl.

8. The process as claimed in any one of claims 1 to 7, characterized in that the diluent (C) exhibits a boiling point B.p. $\geq 100^{\circ}\text{C}$ at standard atmospheric pressure and a viscosity at 25°C $\eta \leq 100 \text{ mPa.s.}$

9. The process as claimed in any one of
claims 1 to 8, characterized in that, prior to stage 1,
the support to be coated is covered using an adhesion
20 primer of the type of those comprising at least one
compound chosen from the group consisting of:

- alkoxylated silanes carrying at least one ethylenic unsaturation and/or at least one epoxide

functional group,

- (meth)acrylates,
- metal chelates and/or alkoxides,
- crosslinkable silicone compositions and
- compositions which are precursors of silicone elastomers.

$$E^{x^0} A_1$$

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